



Effects of demineralization on phenols distribution and formation during coal pyrolysis



Yonghui Bai, Lunjing Yan, Guanlong Li, Ruifang Zhao, Fan Li*

State Key Laboratory Breeding Base of Coal Science and Technology, Co-founded by Shanxi Province and the Ministry of Science and Technology, Taiyuan University of Technology, Taiyuan 030024, China

HIGHLIGHTS

- Effect of inherent mineral on phenols formation during coal pyrolysis was studied.
- Demineralized coal pyrolysis yields higher concentration of phenols.
- Mineral has catalytic activity on the conversion of catechol to phenol.

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ABSTRACT

Phenolic compounds from coal tar are precious chemicals, and the inherent mineral has important impacts on coal tar yields and composition during pyrolysis. Further understanding of the influence of mineral on phenols distribution and formation during coal pyrolysis is of vital importance. In this work, HCl–HF acid-washing was used to pre-treat the raw coals. The pyrolysis behaviors of three coals ranging from lignite to anthracite and their acid-washing residues were analyzed by thermal gravimetric analysis (TGA). The influences of the metals removal on the phenolic compounds yields and distribution were revealed by pyrolysis–GC/MS (Py–GC/MS). Results indicate that demineralization does not change the coal structure. Samples pyrolyzed between 500 °C and 900 °C demonstrate that the total yields of phenol, o-cresol, m/p-cresol, 2,4-xyleneol, 3,4-xyleneol, 2,5-xyleneol, 2,6-xyleneol, β-naphtha, and catechol reach the maximum at 700 °C for both the raw coals and residues. The total phenol yields of residue samples are higher than that of raw samples. The generation of catechol has an obvious dependency on minerals within 700 °C while minerals could influence the phenol and m/p-cresol yields significantly at relatively higher temperatures. It seems that minerals could promote the conversion of relatively bigger phenolic compound to smaller one. Fe₂O₃ and CaO catalyzed model catechol pyrolysis indicate that minerals were helpful to the crack of side chains of catechol and generation of smaller phenol.

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1. Introduction

Before the crude oil became inexpensive in the 1950s and 1960s, coal tar was widely processed to make organic chemicals and liquid fuels, and [1] coal tar may regain its former role as a liquid feedstock with increasing crude oil prices. Pyrolysis is one of the commonly used methods to produce liquid feedstock from coal. Minerals are known to be of importance in coal tar formation process and this has led to research of the effect of inherent minerals in pyrolysis.

In previous studies, acid-washing has usually been used to obtain the demineralized coal to compare the pyrolysis process

with that of raw coal [2–5]. Sathe et al. [6] performed the Loy Yang raw coal and (alkali and alkaline earth metallic species) AAEM removed coal pyrolysis experiments in a wire-mesh reactor at atmospheric pressure with a heating rate of 1 °C/s and 1000 °C/s, found that the tar yields of acid-washing coal are 20% (daf) and 37% (daf) respectively, while the yields for raw coal were 9% (daf) and 20% (daf). Hayashi et al. [7] discovered that the tar yields of AAEM removed coal by acid-washing was 6% higher than that of raw coal when performing the Morwell coal pyrolysis in a CPR reactor with a heating rate of 3000 °C/s at ambient pressure. In brief [8–11], the results from a large number of scholars indicate that the increasing tar yields after demineralization are mainly attributed to the cross-linking effects of AAEM, especially the divalent ions serve as bonds between carboxylic groups in coal matrix. Obviously, inherent

* Corresponding author. Tel.: +86 351 6018076; fax: +86 351 6010482.

E-mail address: lifan66@hotmail.com (F. Li).

mineral matter in coal has significant effect on the yield of coal tar from coal pyrolysis.

As a kind of widely used and high added value chemical products, phenolic compounds are the main components of coal tar. Based on mentioned backgrounds, it is easy to understand the mineral matter may have important effects on the phenolic compounds during coal pyrolysis. But to the best knowledge of the authors, previous studies covering the effect of mineral on phenols distribution and formation during coal pyrolysis is really sparse.

So, in this work, three Chinese coals with ash washed by HCl–HF were prepared and the influence of acid washing on mineral matter content and composition were evaluated. Then the effects of mineral on the coal pyrolysis behavior and phenols distribution were investigated using Py–GC/MS and TGA. The phenols that investigate here are the nine main components in low and middle temperature coal tar, including phenol, m-cresol, o-cresol, p-cresol, 2,4-xyleneol, 3,4-xyleneol, 2,5-xyleneol and 2,6-xyleneol, β -naphthol and catechol.

2. Experimental

2.1. Sample preparation and analysis

Different rank coals including XM (Ximeng lignite from Inner Mongolia), YN (Yining bituminous coal from Xinjiang province), and JC (Jincheng anthracite from Shanxi province) were used in this study. The material (air-dried basis) was ground and sieved to a particle size smaller than 0.2 mm before analysis. Proximate and ultimate analyses of the feedstock were shown in Table 1, which was determined by a combination of China standard methods as described elsewhere [12].

2.2. Acid-washing of coals

The detailed acid-washing procedure of the coals and ash analysis can be found in our previous work [13]. The final demineralized coal samples from XM, YN, and JC were marked as AWXM, AWYN, and AWJC, respectively. The raw coal and demineralized coal were incinerated according to China Standard GB-T/483. The ash was then dissolved by HF and HClO₄. The solution was analyzed for metals by atomic absorption spectroscopy (AAS) according to China Standard GB-T1574. Table 2 shows the metals of the three raw coals and their HCl–HF washing residues determined by AAS. The data show that Fe, Ca, Mg, K, and Na are the main metal elements in the coal ash. YN contains a comparatively higher level AAEM content when compared with XM and JC. Pre-treatment process removes an extremely large proportion of the inorganic matter.

2.3. Py–GC/MS and TG analysis

Py–GC/MS analysis was performed on a CDS analytical pyroprobe 5250 pyrolyzer connected to the FOCUS gas chromatograph and the DSQII mass spectrometer (Thermo Fisher, USA). As know

Table 2

Metal analysis of samples using AAS (dry basis).

Samples	Metal concentration (ppm)					
	XM	AWXM	YN	AWYN	JC	AWJC
Fe	7088	1286	18,029	4142	1590	59
Ca	5696	585	14,049	469	2090	86
Mg	3157	1024	3354	191	491	35
K	2809	75	403	6	152	1
Na	2926	287	932	10	853	4
Mn	109	4	281	3	17	0

[14], the chromatographic peak area of a product is considered linear with its quantity, and the peak area% is linear with its content. Therefore, for each phenolic compound, the changing of its yield before and after pre-treatment in acid can be compared by determining its average peak area. Since the ash contents of the raw coals are rather different from the demineralized samples, 1.01 mg XM and 0.80 mg AWXM, 1.02 mg YN and 0.94 mg AWYN, 1.01 mg JC and 0.92 mg AWJC, were used in pyrolysis experiments to ensure the organic component contents in raw coal and acid-washing sample were the same.

Each sample was pyrolyzed in multi-steps temperature (500 °C, 600 °C, 700 °C, 800 °C, 900 °C, 1000 °C), each for the same residence time (15 s), with the same heating rate of 10 °C/ms, and GC runs automatically under each temperature step. The pyrolysis products were separated on a TG-5MS capillary column (30 m \times 0.25 mm \times 0.25 μ m). Helium (99.999%) was used as the carrier gas, with a constant flow rate of 1 mL/min. The injector temperature was 250 °C, and the column temperature was kept at 50 °C for 3 min, and then increased at 3 °C/min to 300 °C, held for 1 min. The analysis was performed in the SIM mode in the mass spectrometer which had high selectivity and sensibility for the Phenols. The mass spectrometer was operated in EI mode at 70 eV, and the ion source temperature was set to 250 °C.

The TG experiments were performed in the thermogravimetric analyzer (NETZSCH STA449F3), the maximum temperature error of the measurement is ± 1 °C and the mass precision is 1 μ g. Approximately 15 mg initial sample was fed into the Al₂O₃ plate and heated from room temperature to 1000 °C at a constant heating rate of 25 °C/min under Argon atmosphere at a constant flow rate of 50 mL/min.

3. Results and discussions

3.1. Effect on pyrolysis reactivity

The wt% of Fe, Mg, K, Na, and Ca removed from XM, YN, and JC are illustrated in Fig. 1. For samples YN and JC, over 90% of Mg, K, Na, and Ca are removed. Since XM has the highest ash content among the three raw coals, its AAEM removal rate is relatively low when compared with YN and JC. As the dominant metal in all three coals, the removal rate of iron is relatively low compared with other elements.

Table 1

Proximate and ultimate analyses of the coal samples used in the experiments.

Sample	Proximate analysis (wt/%)			Sample	Proximate analysis (wt/%)		
	M_{ad}	A_{ad}	V_{daf}		M_{ad}	A_{ad}	V_{daf}
XM	8.2	20.5	47.1	AWXM	8.9	1.1	45.8
YN	12.6	6.2	33.8	AWYN	11.0	0.9	32.6
JC	0.5	10.1	6.8	AWJC	1.65	0.2	6.7

Note: ad, air-dried basis; daf, dry and ash-free basis.

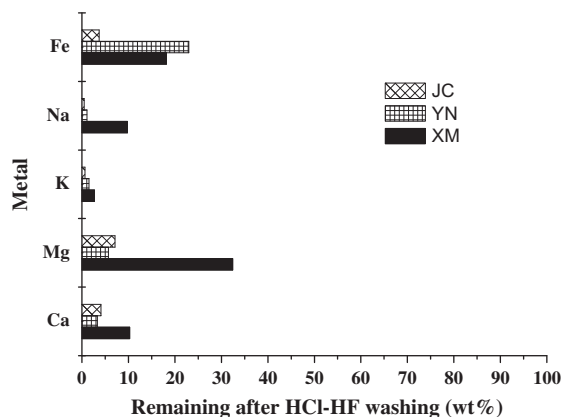


Fig. 1. Removal of Alkali earth metals by pre-treatment in acid.

The effects of the inherent minerals on the weight loss between 200 and 1000 °C during coal pyrolysis as a function of temperature are shown in Fig. 2. The organic matter conversion of all samples increased with increasing pyrolysis temperature. The final mass loss weight of XM, YN, and JC is 42.8%, 33.9%, and 9.5% respectively, suggesting that lignite has the highest pyrolysis reactivity among the three coals while anthracite has the lowest one. In addition, the dry ash free basis pyrolysis conversion of the three raw coals are almost the same as the corresponding demineralized samples, obviously, the inherent mineral matter in coal has little effect on the pyrolysis reactivity, which means the structure change of the coal caused by acid-washing could be ignored [15]. Wang also got the conclusion that HCl–HF washing nearly had no effects on the coal chemical structure by using FT-IR characterization of the lignite used in this study with the same demineralization procedure. Moreover, some other investigations [16–19] on a variety of coals also demonstrate that inherent minerals in coal have little influence on pyrolysis reactivity. It can also be seen from Fig. 2 that the weight loss of the three demineralized coal are all somewhat higher than that of raw coal, about 1.6%, 1.52%, and 0.15% for XM, YN, and JC respectively [20]. Slaghuys deemed that this was mainly attributed to the decomposition of the mineral itself at high temperature.

3.2. Effects on yields and distribution

3.2.1. Effects of mineral on phenols yields

To reveal the effects of minerals, the acquisition of the overall yields of the nine phenols before and after acid treatment are of great significance. Fig. 3 shows the integrated peak areas of the nine phenolic compounds in the chromatograms from the fast pyrolysis of three different coals and their acid-washing residues. With increasing pyrolysis temperature from 500 to 900 °C, the total yields of nine phenolic compounds first increased, and reached a maximum value at 700 °C, then decreased regardless of coal rank and pre-treatment. The main temperature range that phenolic compounds release is between 600 °C and 800 °C which is 100 °C higher than the literature report [21]. The main reason is that rapid heating does not allow completion of each stage at or near the same temperature as in slow heating. The heating rate of the pyrolysis apparatus in this study is 10,000 °C/s which make the onset and active decomposition temperature delayed [22].

Moreover, the total phenol yields of demineralized samples are always higher than that of raw samples. Removal of the mineral matter was prone to greatly promote the total release amounts of the nine phenolic compounds [23]. Kershaw discovered that the introduction of the ion-exchangeable AAEM species was found

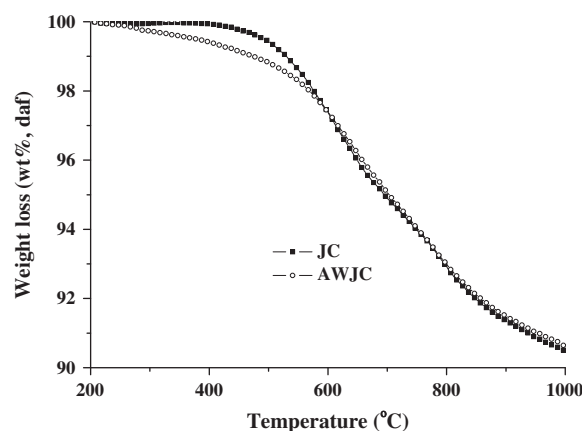
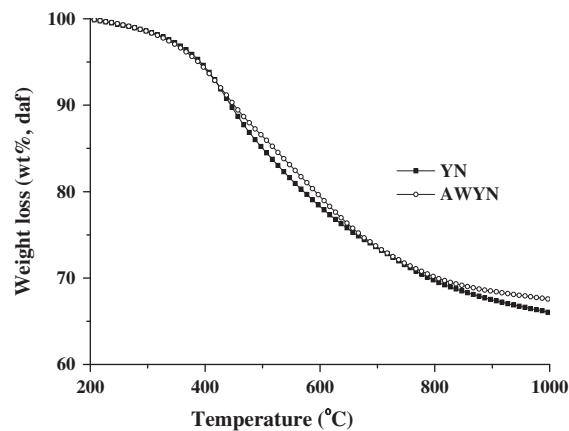
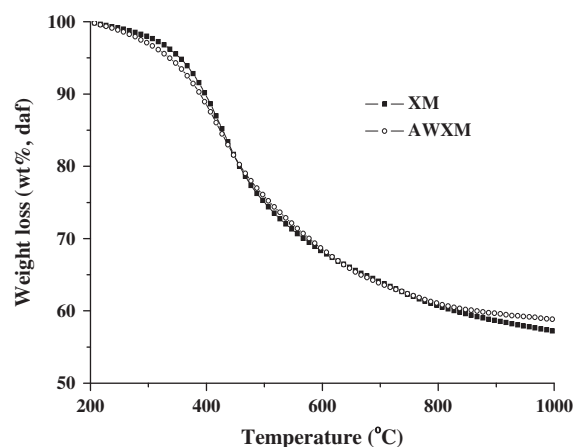


Fig. 2. TGA profiles of raw coal and their acid-washing residues at a rate of 25 °C/min in Ar atmosphere.

to greatly hinder the release of aromatic ring during pyrolysis [24]. With the diminishing of AAEM species, the cross-linking density in the coal/char matrix due to the AAEM cations diminishes rapidly, the corresponding result is that the tar precursors can be released as a big fragment without losing the more aliphatic components, leading to the increased tar yield at high temperatures. It may be that the increasing big fragment contents lead to the higher phenolic compounds yields.

To JC, the phenols yields during pyrolysis are extremely low because of the low oxygen content and high coal rank. Table 1 indicates that the oxygen content of JC is only 5.6% (daf). So, in the following part, the discussion is mainly focus on XM and YN.

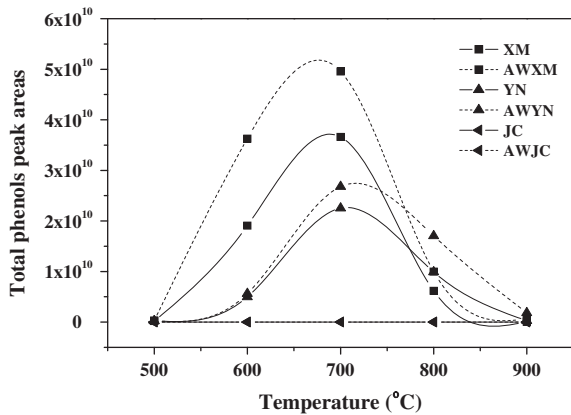


Fig. 3. Total peak areas of nine phenolic compounds during raw coal and their acid-washing residues pyrolysis at different temperatures.

Moreover, it can be seen that the influence of mineral on phenol yields of lignite mainly happens at low temperatures while that happens at relative high temperatures for bituminous coal. Also it shows that when the pyrolysis temperature exceeds 770 °C, the phenol yields of YN are even higher than that of XM.

3.2.2. Effects of mineral on phenolic compounds distribution

Fig. 4 shows the detailed yields distribution of nine phenolic compounds during XM, YN as well as their acid-washing residues

pyrolysis at different temperatures. It can be seen that the presence of mineral has important influence on the phenols distribution. Phenol, o-cresol, m/p-cresol, 2,4-xyleneol, and catechol are the most abundant products for both raw samples and residue samples. For XM lignite, the main temperature range for phenolic compound release is within 700 °C while the range for YN bituminous coal is over 700 °C. This is the reason that the influence of mineral on phenol yields of lignite mainly happens at low temperatures while that happens at relative high temperatures for bituminous coal. Moreover, almost all phenolic compounds were occurred in products of coal pyrolysis until temperature reached 600 °C and 800 °C, which demonstrated that the release of phenolic compounds is in favor of medium temperature, just as the result in literature [25].

For both YN and XM, the most obvious influence of mineral on phenols production is the dramatically decreased catechol yield. This phenomenon is applicable in the whole temperature range. Especially at 700 °C, the catechol yield during AWXM and AWYN pyrolysis are 4.7 and 8.7 times higher than that of raw coal pyrolysis. Meanwhile, the yield of relatively small phenols decreased obviously. Therefore, it may be that the mineral matter has catalytic effect on the conversion of catechol to phenol, which made the big molecular phenolic compound transformed to relatively small one.

Since 700 °C shows the maximum phenols yields, to understand the transformation path of phenolic compounds in the presence of minerals is important. In the following part, we use pure catechol as model compound to further illuminate the role that mineral plays during coal pyrolysis. Taking catechol as model compound

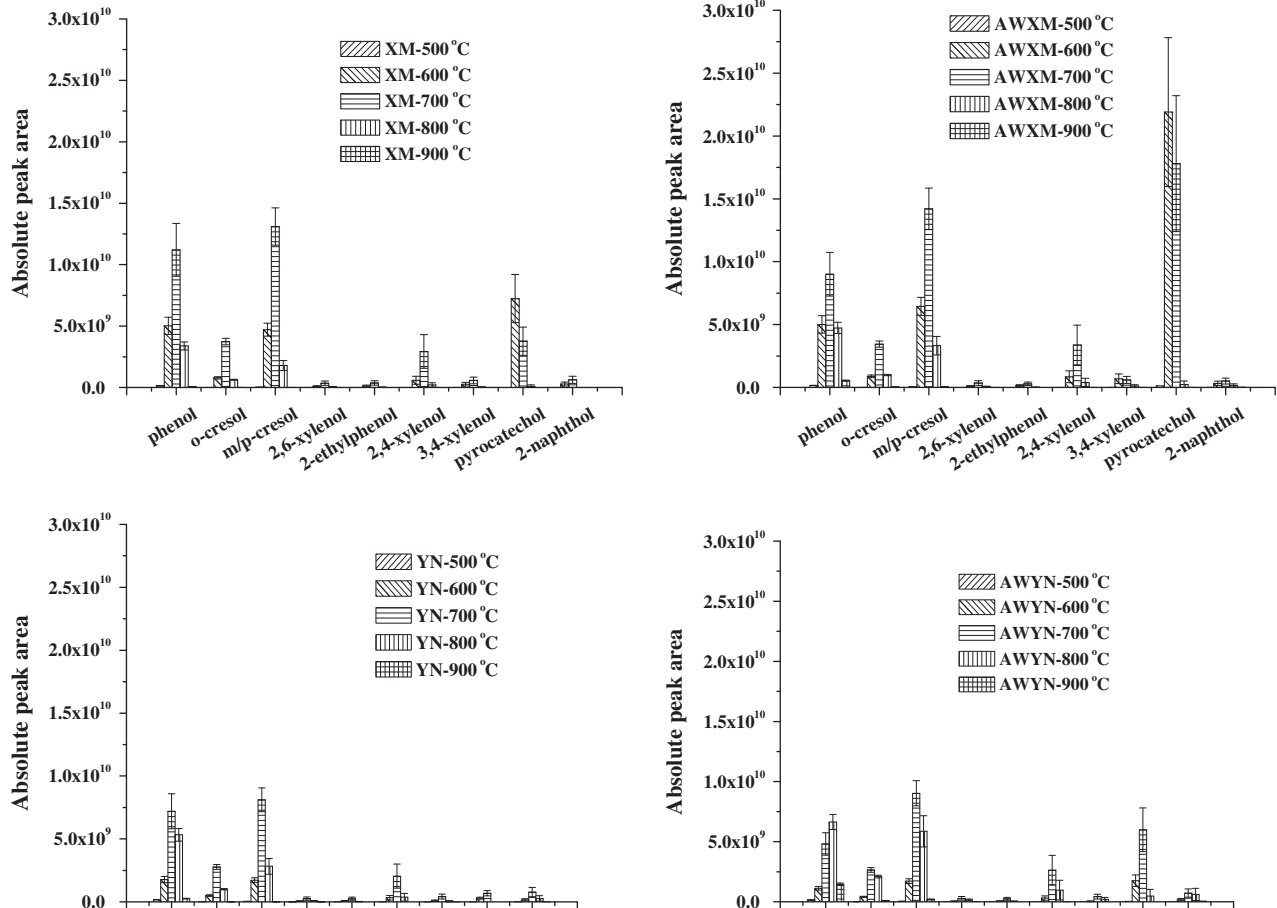


Fig. 4. Peak areas of phenols during raw and demineralized coal pyrolysis.

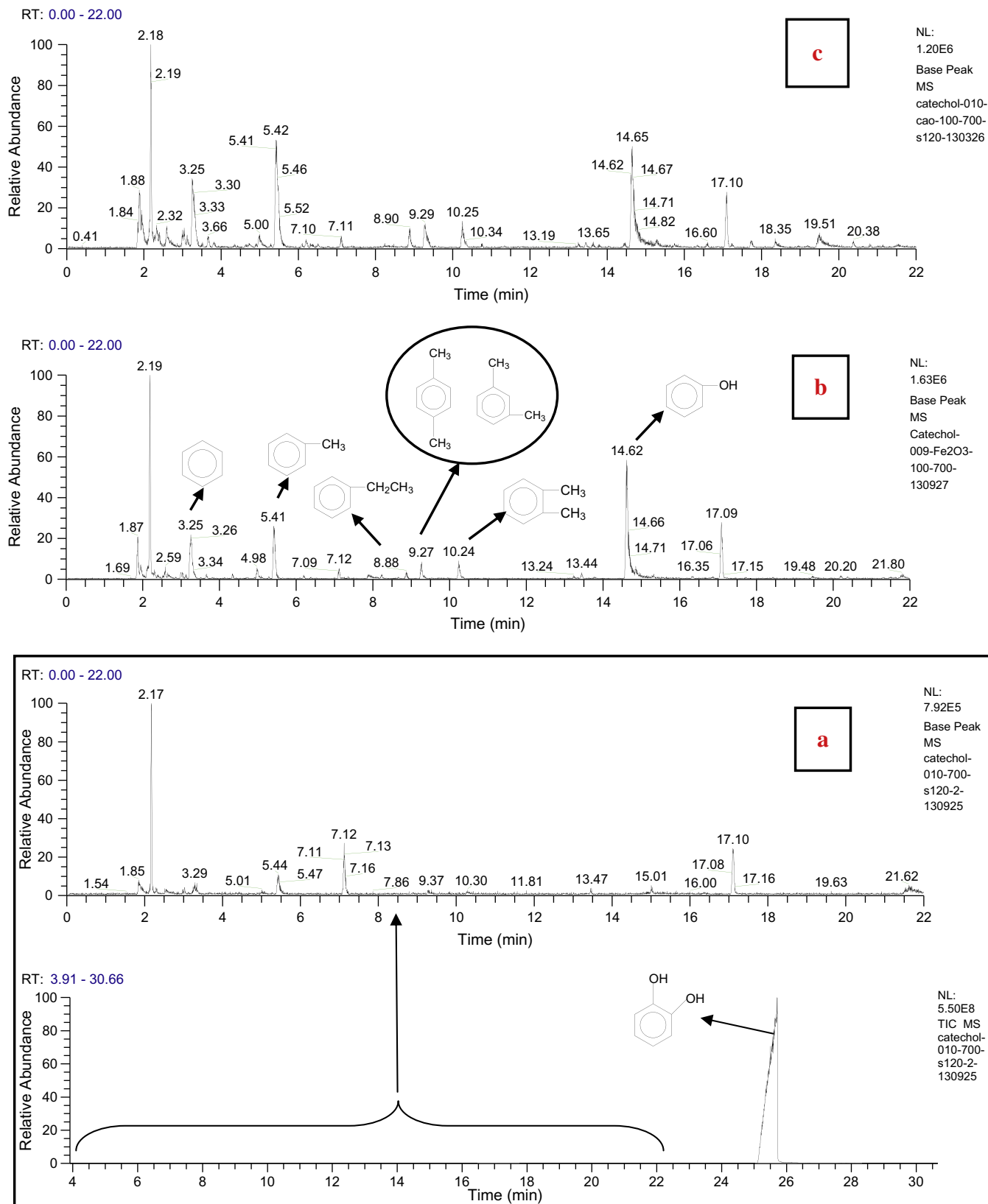


Fig. 5. Full scan chromatograms of catechol and catechol with Fe₂O₃ and CaO added respectively. (a): pure catechol, (b): catechol with Fe₂O₃ added, (c): catechol with CaO added).

has two advantages. One is that it has the most obvious dependency on the presence of mineral. Another is that catechol is a predominant structural entity of solid fuel [26], and catechol is a

suitable model compound for investigating decomposition reaction pathways and their relation to phenolic compound formation during pyrolysis.

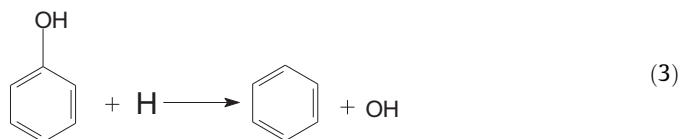
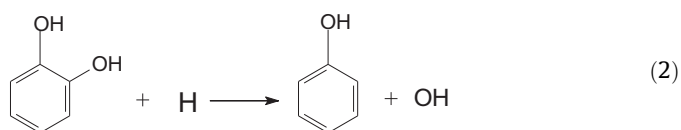
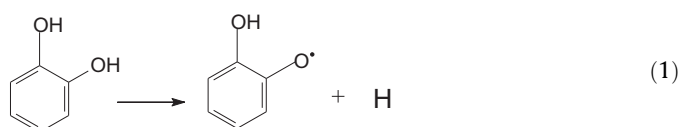
3.2.3. Effects of mineral on phenolic compounds transformation

As stated above, the presence of AAEM species may have important influence on the distribution and formation of phenols. As the most abundant AAEM species in both XM and YN, the content of Ca in them is 5226 and 12,281 ppm, respectively. Fe is the most abundant metal element in both coals. In order to verify the inference that the mineral matter has catalytic effect on the conversion of catechol to phenol, CaO and Fe₂O₃ catalyzed pure catechol pyrolysis at 700 °C were performed. Fig. 5 shows the full scan chromatograms of pyrolysis product of catechol and catechol with CaO and Fe₂O₃ added respectively. Compounds have been identified using a combination of a mass spectral database and retention data for standard components.

Fig. 5a shows the products from the pure catechol pyrolysis. The benzene and methylbenzene with lower intensity was found at retention time, 5.44 and 3.29 min, respectively. Based on spectrogram, the peaks at the retention time of 2.18 and 17.10 min are caused by column bleeding itself but not products generated from the pyrolysis of catechol. The bottom figure also shows that the catechol peak after pure catechol pyrolysis at 700 °C is still extremely high. This demonstrates that catechol is thermally stable and could not decompose easily without the addition of catalyst. Compared with pure catechol pyrolysis, Fig. 5b shows that Fe₂O₃ + catechol generates some new products which were reflected by the phenol peak appeared around retention time 14.62 min, meanwhile, around 9.29 min, m/p-cresol was found, around 10.25 min o-xylene was found, around 8.9 min ethylbenzene was found. Besides, the methylbenzene and benzene peak, respectively, at original retention time of 5.44 and 3.25 min were obviously strengthened. The highest relative abundance intensity is 1.63×10^6 . The category of products generated by the pyrolysis process of CaO + catechol is the same with Fe₂O₃ + catechol but the content is obviously different. By initially compare among Fig. 5a–c, it can be found that in the presence of metal oxide, catechol can be decomposed into small molecules mainly including benzene and phenol.

To quantitatively reveal the difference of catalysis of CaO and Fe₂O₃, Fig. 6 gives the influence of the adding of metal oxide on the absolute peak area of the main products from catechol pyrolysis at 700 °C. It can be found that CaO and Fe₂O₃ have important influence on the formation and distribution of products from catechol pyrolysis, and the catalysis performance of CaO is more evident than that of Fe₂O₃. Especially, the generation of phenol is seriously depending on the adding of CaO and Fe₂O₃. After adding CaO or Fe₂O₃, the phenol content generated from catechol pyrolysis is as much 61 times and 56 times, respectively as direct

pyrolysis of pure catechol. Besides, CaO can improve the generation of m/p-cresol but Fe₂O₃ cannot.



From the information about the decomposition of phenolic compound in other studies [27,28], the first step of the catechol decay is most likely to be the scission of an O–H bond, a hydroxy-substituted phenoxy radical and H atom are formed, show in Eq. (1). Then the H atom reacts with catechol, yielding phenol and the OH radical, showed in Eq. (2). Benzene is generated from phenol via the displacement of OH by an H atom, showed in Eq. (3). Wang et al. [29] think that the CaO surface base sites could activate hydroxyl through the abstraction of H⁺, which could promote the generation of O^{δ-}. It is maybe that at the circumstance of the high temperature, with the existing of CaO, the strong alkaline O²⁻ can activate catechol, thus generate negative charges of atom O on the phenolic hydroxyl. Therefore, generated proton can react with catechol via replacing hydroxyl to form phenol. Based on this, the adding of alkaline metal oxide can increase the content of phenol. The analysis results show that minerals in coal have important influence on the phenols distribution and formation, which in turn affect the yield of the coal tar and composition.

4. Conclusions

This work was conducted to gain more information about the role that the inherent mineral played on phenols formation and transformation during coal pyrolysis since the obtained knowledge would provide guidance for the acquisition of precious phenols from coal tar more effectively.

The release of phenolic compounds is in favor of the temperature range of 600 °C and 800 °C. Pyrolysis at 700 °C gives the highest yields of phenolic compounds for both raw coal and acid-washing residues. The total phenols yields from residues pyrolysis are always higher than that from raw samples. The most obvious influence of minerals removal posed on phenols production is the dramatically increased catechol yield. At 700 °C, the catechol yield during AWXM and AWYN pyrolysis are 4.7 and 8.7 times higher than that of raw coal pyrolysis. The mineral matter has catalytic activity on the decomposition of catechol. The big molecular phenolic compound could be transformed to relatively small one in the presence minerals. Ca and Fe species play a critical role in this process.

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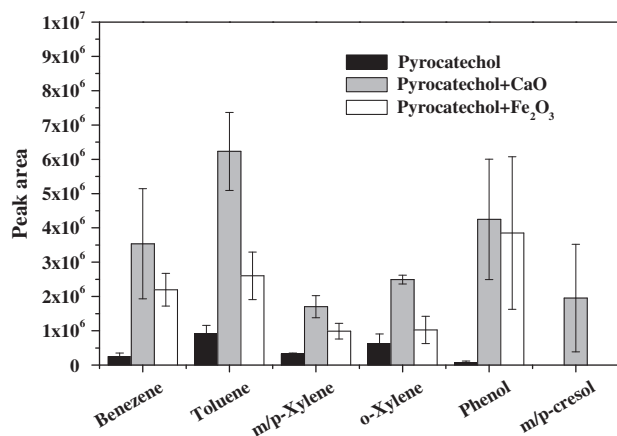


Fig. 6. Effect of CaO and Fe₂O₃ on the decomposition of catechol at 700 °C.

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References

- [1] Bell DA, Towler BF, Fan MH. Coal gasification and its applications. 1st ed. Great Britain: Elsevier Inc.; 2011.
- [2] Öztaş NA, Yürüm Y. Pyrolysis of Turkish Zonguldak bituminous coal. Part 1. Effect of mineral matter. *Fuel* 2000;79:1221–7.
- [3] Yürüm Y, Dror Y, Levy M. Effect of acid dissolution on the mineral matrix and organic matter of Zefa Efe oil shale. *Fuel Process Technol* 1985;11:71–86.
- [4] Karabakan A, Yürüm Y. Effect of mineral matrix in the reactions of oil shales: 1. Pyrolysis reactions of Turkish Göynük and US Green River oil shales. *Fuel* 1998;77:1303–9.
- [5] Karabakan A, Yürüm Y. Effect of mineral matrix in the reactions of oil shales: Part 2. Oxidation reactions of Turkish Göynük and US Western Reference oil shales. *Fuel* 2000;79:785–92.
- [6] Sathe C, Hayashi JI, Li CZ, Chiba T. Combined effects of pressure and ion-exchangeable metallic species on pyrolysis of Victorian lignite. *Fuel* 2003;82:343–50.
- [7] Hayashi JI, Amamoto S, Kusakabe K, Morooka S. Flash pyrolysis of brown coal modified by alcohol-vapor explosion treatment. *Energy Fuels* 1996;10:1099–107.
- [8] Tyler RJ, Schafer HNS. Flash pyrolysis of coals: influence of cations on the devolatilization behaviour of brown coals. *Fuel* 1980;59:487–94.
- [9] Wornat MJ, Nelson PF. Effects of ion-exchanged calcium on brown coal tar composition as determined by Fourier transform infrared spectroscopy. *Energy Fuels* 1992;6:136–42.
- [10] Cliff DI, Doolan KR, Mackie JC, Tyler RJ. Products from rapid heating of a brown coal in the temperature range 400–2300 °C. *Fuel* 1984;63:394–400.
- [11] Srinivasachar S, Helble JJ, Ham DO, Domazetis GA. A kinetic description of vapor phase alkali transformations in combustion systems. *Prog Energy Combust Sci* 1990;16:303–9.
- [12] Dong J, Li F, Xie KC. Study on the source of polycyclic aromatic hydrocarbons (PAHs) during coal pyrolysis by PY–GC–MS. *J Hazard Mater* 2012;243:80–5.
- [13] Bai YH, Wang YL, Zhu SH, Yan LJ, Li F, Xie KC. Synergistic effect between CO₂ and H₂O on reactivity during coal chars gasification. *Fuel* 2014;126:1–7.
- [14] Lu Q, Zhang ZB, Yang XC, Dong CQ, Zhu XF. Catalytic fast pyrolysis of biomass impregnated with K₃PO₄ to produce phenolic compounds: Analytical Py–GC/MS study. *J Anal Appl Pyrolysis* 2013;104:139–45.
- [15] Wang MJ, Fu CH, Chang LP, Xie KC. Effect of fractional step acid treatment process on the structure and pyrolysis characteristics of Ximeng brown coal. *J Fuel Chem Technol* 2012;40:906–11.
- [16] Liu QR, Hu HQ, Zhou Q, Zhu SW, Chen GH. Effects of inorganic matter on reactivity and kinetics of coal pyrolysis. *Fuel* 2004;83:713–8.
- [17] Chen HK, Li BQ, Zhang BJ. Effects of mineral matter on products and sulfur distributions in hydrolysis. *Fuel* 1999;78:713–9.
- [18] Franklin HD, Peters WA, Howard JB. Mineral matter effects on the rapid pyrolysis and hydrolysis of a bituminous coal. 1. Effects on yields of char, tar and light gaseous volatiles. *Fuel* 1982;61:155–60.
- [19] Franklin HD, Peters WA, Howard JB. Mineral matter effects on the rapid pyrolysis and hydrolysis of a bituminous coal. 2. Effects of yields of C₃–C₈ hydrocarbons. *Fuel* 1982;61:1213–7.
- [20] Slaghuys JH, Ferreira LC, Judd MR. Volatile material in coal: effect of inherent mineral matter. *Fuel* 1991;70:471–3.
- [21] Nola GD, Jong WD, Spliethoff H. TG–FTIR characterization of coal and biomass single fuels and blends under slow heating rate conditions: partitioning of the fuel-bound nitrogen. *Fuel Process Technol* 2010;91:103–15.
- [22] Rafael K, Alan H, Keith B. Solid fuels and heavy hydrocarbon liquids. London: Elsevier Science; 2006. p. 37–90 [chapter 3].
- [23] Kershaw JR, Sathe C, Hayashi JI, Li CZ, Chiba T. Fluorescence spectroscopic analysis of tars from the pyrolysis of a Victorian brown coal in a wire-mesh reactor. *Energy Fuels* 2000;14:476–82.
- [24] Li CZ, Sathe C, Kershaw JR, Pang Y. Fates and roles of alkali and alkaline earth metals during the pyrolysis of a Victorian brown coal. *Fuel* 2000;79:427–38.
- [25] Blazsó M, Jakab E. Study of thermal decomposition reactions in coals by pyrolysis–gas chromatography–mass spectrometry. *J Anal Appl Pyrolysis* 1985;8:189–94.
- [26] Lynch BM, Durie RA. Comparative studies of brown coal and lignin. II. The action of concentrated alkali at elevated temperatures. *Aust J Chem* 1960;13:567–81.
- [27] Brezinsky K, Pecullan M, Glassman I. Pyrolysis and oxidation of phenol. *J Phys Chem A* 1998;102:8614–9.
- [28] Christof H, Karin R, Peter F, Thomas J. Shock-tube study on the high-temperature pyrolysis of phenol. *Symp Combust Inst* 1998;27:321–8.
- [29] Wang DF, Zhang XL, Wei W, Sun YH. Synthesis of diethyl carbonate from ethyl carbamate and ethanol over basic oxide catalysts. *Petrochem Technol* 2012;41:396–400 [in Chinese].